

Charge critical fluctuations in cuprates: Isotope effect, pseudogap, conductivity and Raman spectroscopy

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Abstract

Within the stripe quantum critical point theory for high T_c superconductors, we point out that there is a direct contribution of charge collective fluctuations to the optical absorption and to the Raman spectra. In this latter case, we find that the critical charge collective modes can or can not be excited depending on the direction of their wavevector and on the polarization of the incoming and outgoing photons. This indicates a marked distinction between quasiparticles which are strongly and weakly coupled to critical collective modes and provides a direct confirmation that the order associated to the quantum critical point near optimal doping of cuprates occurs at finite wavevectors.

Key words: High T_c superconductivity, stripe quantum critical point, Raman spectroscopy, optical conductivity
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1. Introduction

The discovery of metallic systems like the high-temperature superconducting (SC) cuprates and some heavy-fermion compounds violating the standard Landau theory of Fermi-liquid (FL) is one of the most remarkable issues of condensed matter. All these anomalous metals are characterized by large electron-electron correlations and by the proximity to some electronic instability. These latter features are naturally related: Once the strong correlations reduce the electron kinetic energy of the propagating, coherent metallic excitations (the FL quasiparticles, QP), the system is more prone to “secondary” interactions (magnetic, phononic,...), which favor ordered phases (most commonly magnetic, but also stripes, or orbitally ordered). If these instabilities take place as a second-order phase transition, (a quantum critical point, QCP, at $T = 0$) the low-energy critical fluctuations can mediate strong (singular) residual interactions between the FL QP, which lose their stability and FL is spoiled. A QCP would be a

crucial ingredient of the non-FL behavior and possibly also of high temperature SC. For cuprates, besides early theoretical suggestions [1,2], there are many experimental confirmations [3,4,5,6,7,8] that a QCP is “hidden” near optimal doping below the SC dome. This QCP would be the end-point of a critical line below which an ordered or nearly ordered phase takes place in the underdoped region and it is made manifest below the SC dome when SC is suppressed. One first question regards the nature of this ordered state. Besides the intrinsically elusive (and controversial [9]) character of the ordered phase with order at zero wavevector and time-reversal breaking [13] there is the more “traditional” possibility that the ordered state is a state with charge (and spin) modulations at a finite wavevector \mathbf{q}_c (charge-ordered (CO) stripe phase). There are many experimental evidences that this state is realized in the cuprates [3,14,15]. Of course this state could be established only on a local (and possibly dynamical) basis [11,12] due to the competition with other mechanisms (like pairing and quenched disorder) [20].

As a consequence of critical charge fluctuations

at \mathbf{q}_c , only some portions of the Fermi surface (the so-called “hot spots”) are connected by these specific wavevectors at low energy. Momentum conservation imposes that only “hot” QP are strongly scattered, while the other portions of the Fermi surface are still weakly interacting (“cold” QP). Therefore, the very existence of distinct “hot” and “cold” QP by itself indicates that the (nearly) ordered state is at a finite wavevector. Indeed, from the experimental point of view, there are evidences that QP on the Fermi surface of cuprates do have quite different scattering rates. For instance, recent angle-resolved photoemission spectroscopy (ARPES) experiments [10] give evidence of a superlinear behavior in ω and T for the scattering rate of nodal QP even in the pseudogap state of an underdoped Bi2212 sample. Recent Raman scattering experiments also show different behaviors depending on the photon polarizations, which probe different regions of the fermionic k -space, in agreement with a \mathbf{q}_c suitable for the stripe phase. This will be a main point of the present work reiterating that these different behaviors are only possible in the presence of strong scattering at specific *finite* wavevectors. We show how the critical (i.e., low-energy) charge fluctuations at finite \mathbf{q}_c directly contribute to the spectral properties. A quite similar perspective was long ago assumed by Aslamazov and Larkin for the paraconductivity due to SC pair fluctuations above the critical temperature in traditional SCs [16] and by Patton and Sham [17] for one-dimensional systems near a charge-density-wave transition.

2. The “Stripe” Quantum Critical Point in the cuprates

A charge-ordering second-order instability [2,3] was shown to occur in many models of strongly correlated electrons and a detailed analysis was carried out on a Hubbard-Holstein model. The tendency to phase separation of these strongly correlated electrons is opposed by their charged character. In this way the Coulombic repulsion prevents thermodynamic phase separation, but leaves open the possibility of charge segregation on a microscopic scale[19]. The direct analysis of the model for realistic parameters revealed a charge-density wave (CO) phase in a substantial region of the phase diagram below a doping-dependent critical temperature $T_{CO}(x)$ ending at zero temperature in a QCP around optimal doping. Actually a typical value for the critical doping

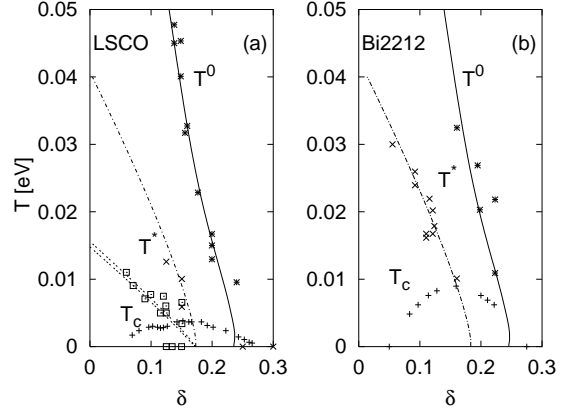


Fig. 1. From Ref. [11]: Temperature vs. doping δ phase diagram of the cuprates according to the CO-QCP scenario for LSCO (a) and Bi2212 (b). The solid line is the mean-field critical line ending at $T = 0$ in the mean-field QCP at $\delta_c^{(0)}$. The dashed lines mark the critical lines in the presence of fluctuations, ending in the QCP at δ_c . Steeper lines correspond to “critical lines” detected by “faster probes”. For details see Ref.[11]. The experimental points for T^0 (*) and for T^* measured with fast (x) and slow (□) probes for LSCO are from Ref.[22], those for Bi2212 are from Refs.[23]. The experimental critical temperatures T_c are also shown (+).

of the QCP, $x_c = 0.19$, was theoretically predicted [2] before the many experimental evidences for a QCP precisely at this doping were published [4]. As a consequence of the proximity to a CO critical line, singular interactions arise and strongly influence the physical properties. In particular, we found that approaching the T_{CO} transition, strong CO fluctuations may mediate pairing in the d -wave channel [2,12] despite the non-magnetic character of the interaction. Then pair formation, as well as disorder and low-dimensionality prevent the actual occurrence of long-range CO. More recently we accounted for the existence of *two* different crossovers below which pseudogaps open. Below the crossover at higher temperature (T^0) weak pseudogaps opens in experiments probing the overall electronic DOS, while according, e.g., to ARPES, stronger pseudogaps open below a lower crossover temperature T^* [11]. Formally T^0 arises from a mean-field calculation and it corresponds to the temperature T_{CO}^0 at which the system would undergo a CO transition if the fluctuations were not relevant. However, fluctuations do play a relevant role: An obvious effect of CO fluctuations is to open (weak) pseudogaps which may be revealed by experiments detecting the electronic DOS (like, e.g., uniform spin susceptibility and specific heat). Including the effect of fluctuations the transition temperature is reduced and shifted at lower doping. This lower transition

temperature T_{CO} is the transition at which the system is expected to order. However, upon approaching T_{CO} , the charge fluctuations mediate pairing and strong Cooper pair fluctuations also appear (as experimentally indicated in [8]). These pairing fluctuations coexist with the *dynamical* charge-order fluctuations and lead to formation of a stronger gap at a temperature $T^* \gtrsim T_{CO}$.

Fig. 1 shows a comparison between the calculated $T^0 = T_{CO}^0$ and $T^* \approx T_{CO}$ with a collection of experimental determinations of these crossover temperatures in two classes of cuprates based on La [Fig. 1(a)] and on Bi [Fig. 1(b)]. It is clear that *two* distinct crossover lines occur, in agreement also with recent redeterminations of the doping levels in cuprates via thermoelectric power experiments [21]. Remarkably, within the same scheme, we qualitatively explained the strong increase of T^* upon isotopic replacement of ^{16}O with ^{18}O observed in some neutron-scattering experiments on Ho-based 124 cuprates [18]. This isotopic effect arises from the phonon-driven instability and crucially involves the presence of substantial CO dynamical fluctuations. Such an effect is highly non trivial: While T^0 is not affected by the isotopic replacement, T^* *increases* upon reducing the frequency of the phonons involving oxygen ions. This effect is much stronger than on the SC T_c , which instead shows a small *decrease*.

The distinct nature of the two pseudogaps is confirmed by recent experiments [21] showing that the two pseudogap lines behave differently upon Zn doping: In the presence of Zn impurities T^* evolves into T^0 . Within our scenario this occurs because Zn suppresses the fluctuations (Zn is a pair-breaker and a pinning center for CO fluctuations). A cross-check would be that, while upon replacing ^{16}O with ^{18}O on the absence of Zn, T^* increases, when Zn impurities are present T^* is replaced by T^0 and no isotopic effect should be observed.

3. Optical and Raman spectra

Having established that strong critical fluctuations are present in a large portion of the phase diagram with non-trivial effects, we shall focus on the effect that CO fluctuations can have providing an *additional* channel for the Raman response, besides the usual one obtained from the FL QP. Later on we will elaborate on the more drastic (and, if realized, revolutionary) possibility that CO fluctuations are so strong near optimal doping that single QP excitations (even with non-FL characetr) are

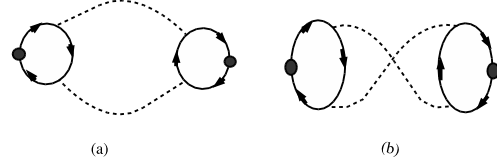


Fig. 2. Direct (a) and crossed (b) Aslamazov-Larkin-like diagrams for the fluctuation contributions to conductivity and Raman spectra. The dots represent current or Raman vertices. Solid lines represent fermionic QP propagators and dashed lines represent CM.

strongly suppressed and the optical properties are mainly determined by the CO fluctuations. These processes are diagrammatically represented by the Raman or current-current response functions of Fig. 2. Contrary to the usual Aslamazov-Larkin (AL) theory of paraconductivity[16], the particle-hole character of the CO modes is such that a cancellation occurs in the current-current response function between the diagram 2(a) and the diagram 2(b) [17,24]. As a consequence, the two AL-like diagrams for CO collective modes (CM) are less singular and do not contribute to transport. Nevertheless, we find here that such a cancellation does not occur for Raman vertices of suitable symmetry and important singular contributions can appear in the Raman response.

— *Raman Response* — Specifically each fermionic loop appearing in the Raman response has the form

$$\Lambda_{\alpha,\beta}(\Omega_l; \mathbf{q}, \omega_m) = CT \sum_n \sum_k \gamma_{\alpha,\beta}(\mathbf{k}) G(\mathbf{k}, \varepsilon_n + \Omega_l) \times G(\mathbf{k} - \mathbf{q}, \varepsilon_n - \omega_m) G(\mathbf{k}, \varepsilon_n), \quad (1)$$

where $\gamma_{\alpha,\beta}(\mathbf{k}) \equiv \partial^2 E_{\mathbf{k}} / \partial k_\alpha \partial k_\beta$ and C is a constant determined by the coupling of the Raman vertex with the incoming and outgoing photons, the coupling of the CO CM with the fermions, and so on. The choice of the α and β components depends on the polarization of the incoming and outgoing photons [25]. A suitable choice of these polarizations corresponds to specific projections of the $\gamma(\mathbf{k})$ vertex on cubic armonics of the square lattice. In this way, for instance, a given polarization choice corresponds to a Raman vertex with B_{1g} symmetry $\gamma_{B_{1g}} = [\cos(ak_x) - \cos(ak_y)]$ (a is the lattice spacing). It is now crucial to notice that, contrary to the current vertices entering the calculation of conductivity, this Raman vertex is even under parity and the above cancellation between the direct and the crossed AL-like diagrams no longer occurs. Moreover we are interested in the most singular contributions, which occur when the CM

are around \mathbf{q}_c . Therefore we set $\mathbf{q} = \mathbf{q}_c$ in Eq. (1), which leads to a dominant contribution when the three fermions are around the hot spots. Therefore in Eq. (1), to avoid cancellations, \mathbf{q}_c must be suitable to connect regions in k-space where the B_{1g} vertex does not change sign. Since $\gamma_{B_{1g}}$ changes sign only under the x vs. y interchange, this is the case for stripes at not too small doping [2,15], where $\mathbf{q}_c \approx (2\pi/a)(\pm 0.21, 0), (2\pi/a)(0, \pm 0.21)$. On the other hand, when the B_{2g} vertex $\gamma_{B_{2g}} = \sin(ak_x)\sin(ak_y)$ is considered in Eq. (1), the leading contribution from hot spots vanishes since, for fixed \mathbf{q}_c the two “available” hot spots give contributions from regions where $\gamma_{B_{2g}}$ is opposite in sign. Roughly speaking, each symmetry “probes” different regions of the fermion k-space. In the case of B_{1g} this region corresponds to the one with hot spots, which can therefore emit and reabsorb critical CM. On the other hand, the fermions excited with B_{2g} symmetry are “cold” and have difficulties in emitting and reabsorbing CM according to the scheme of the diagrams in Fig. 2. Indeed it is found experimentally [26] that the anomalous Raman spectra in $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ are only observed in the B_{1g} symmetry, while the behavior of the B_{2g} can be accounted for by QP only.

We find a CM contribution to B_{1g} Raman scattering given by

$$\Delta\chi'' = \Lambda_{B_{1g}}^2 \int_0^\infty dz [n_B(z - \omega/2) - n_B(z + \omega/2)] \times \frac{z_+ z_-}{z_+^2 - z_-^2} [F(z_-) - F(z_+)] \quad (2)$$

where $n_B(z)$ is the Bose function,

$$F(z) \equiv \frac{1}{|z|} \left[\arctan\left(\frac{\omega_0}{|z|}\right) - \arctan\left(\frac{m}{|z|}\right) \right], \quad (3)$$

and $z_\pm \equiv (z \pm \omega/2)(1 + (z \pm \omega/2)^2/\omega_0^2)$. Here $\omega_0 \sim 200 - 500 \text{ cm}^{-1}$ is some suitable ultraviolet cut-off of the order of the frequency of the phonons most strongly coupled to the electrons and driving the systems CO-unstable. The above expression of $\Delta\chi''$ is calculated by considering critical collective modes with a semiphenomenological spectral density of the form

$$A(\omega, \Omega_{\mathbf{q}}) = \frac{\omega \left[1 + \left(\frac{\omega}{\omega_0} \right)^2 \right]}{\omega^2 \left[1 + \left(\frac{\omega}{\omega_0} \right)^2 \right]^2 + \Omega_{\mathbf{q}}^2} \quad (4)$$

$\Omega_{\mathbf{q}} = \nu|\mathbf{q} - \mathbf{q}_c|^2 + m(x, T)$ is the dispersion law of the nearly critical CM modes, while $m(x, T)$ is the mass of the critical modes and encodes the

distance from the critical line $T_{CO}(x)$, where x is the doping. In the limit of infinite ω_0 , one recovers the spectral density of critical CM, associated to the Matsubara inverse propagator $D^{-1}(\mathbf{q}, \omega_m) = (|\omega_m| + \Omega_{\mathbf{q}})$. In Fig. 3(a) we report a comparison between our theoretical calculations and experimental data from Ref. [26] taken on $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ sample at rather large temperatures. The agreement is manifestly satisfactory, although there are some adjustable parameters.

It is noticeable that the Raman response is driven by a low-energy scale $m(x, T)$. The inset reports the (experimental) position of the peaks $\Omega(x, T)$ and CM mass $m(x = 0.10, T)$ needed to fit the experimental curves: At large to moderate temperatures $m(T)$ has a linear part, which has an intercept on the T axis at a temperature $T^*(x = 0.10) \approx 80 \text{ K}$. At lower temperatures m saturates since the system crosses over to a nearly ordered regime with a finite $m(T)$. This behavior is clearly consistent with the behavior expected for the mass of critical modes in the underdoped region: At large temperatures the system is in the quantum critical regime with $m \propto (T - T^*)$, while below a crossover temperature T^* [which for LSCO at $x = 0.10$ is indeed about $60 - 80 \text{ K}$, see Fig. 1(a)] the CO transition is quenched by other effects (pairing, disordered inhomogeneities, local ordering....) and the mass saturates.

If the singular modes had wavevectors along the diagonal (1,1) and (1,-1) directions and small modulus, the role of the B_{1g} and B_{2g} would be reversed, with this latter displaying the most singular Raman absorption. Noticeably, experiments in $\text{La}_{1.98}\text{Sr}_{0.02}\text{CuO}_4$, where neutron scattering show incommensurate (spin, but likely also stripe) order along the diagonal directions, do show that the anomalous Raman absorption is present in the B_{2g} symmetry and is absent in the B_{1g} . Fig. 3(b) reports a comparison between experimental data of Ref. [26] and a calculated fluctuation contribution for this B_{2g} case. Also in this case the high-temperature linear part of $m(x = 0.02, T)$ has an intercept at a finite $T^* \approx 200 \text{ K}$ which, consistently with the T^* values reported in Fig. 1(a) has a much larger value. After we linearly extrapolate the $T^*(x)$ curve from the two values obtained at $x = 0.02$ and $x = 0.10$, we find that $T^*(x = x_c)$ vanishes for a value $x_c \approx 0.17$ consistent with the position of the CO-QCP of Fig. 1(a) and certainly not inconsistent with most of the experiments.

— *Optical conductivity* — We mentioned above that the particle-hole character of the CO fluctuations results in a cancellation between the two diagrams of Fig. 2 for the current-current re-

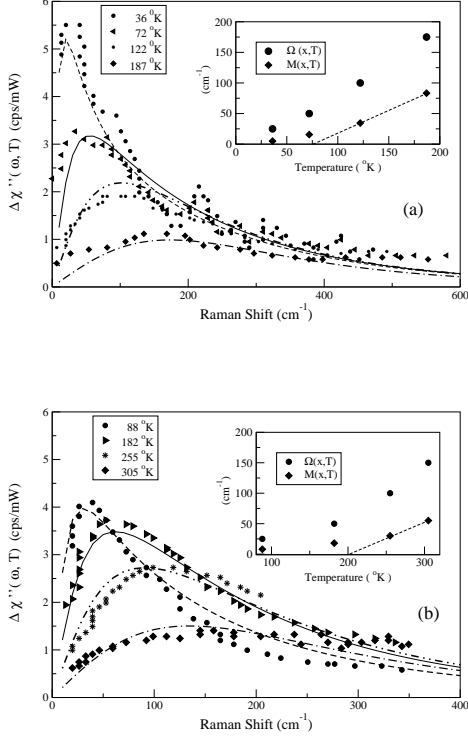


Fig. 3. (a) Comparison between experimental Raman spectra on $\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_4$, and theoretical spectra calculated from diagrams of Fig. 2. The intensity is chosen to fit the data with $\Lambda_{B_{2g}}^2 = 1.7$, the high-frequency cutoff is $\omega_0 = 250 \text{ cm}^{-1}$, and the mass is reported in the inset. (b) Same as (a) for $\text{La}_{1.98}\text{Sr}_{0.02}\text{CuO}_4$ with $\Lambda_{B_{2g}}^2 = 0.85$.

sponse. In two dimensions this would result in non-singular fluctuation contributions to transport and in a finite-frequency absorption of CM, which decreases with temperature, in contrast with optical conductivity data. This might indicate that the neutral (particle-hole) non-dipole-active CO excitations hardly couple with the electromagnetic (e.m.) field and the anomalous transport and optical behavior of the cuprates arises from other processes [27]. However, several mechanisms may be present in real systems, resulting in an effective direct coupling of the e.m. field to the charge modes or (equivalently) in a non complete cancellation between the diagrams of Fig.2 [28]. If this is the case the fluctuation contribution to the optical conductivity can easily be obtained as $\sigma(\omega, T) = C_\sigma \Delta\chi''(\omega, T)/\omega$, where C_σ is a suitable dimensional constant accounting for the effective coupling between CM and the e.m. field. We performed a comparison between recent optical conductivity data [29] with our calculated $\sigma(\omega, T)$ using the strenght C_σ and the high-energy cutoff ω_0 as adjustable parameters (but the same for all temperatures) and varying the CM mass $m(T)$ to fit the curves. The result is reported in Fig. 4 along

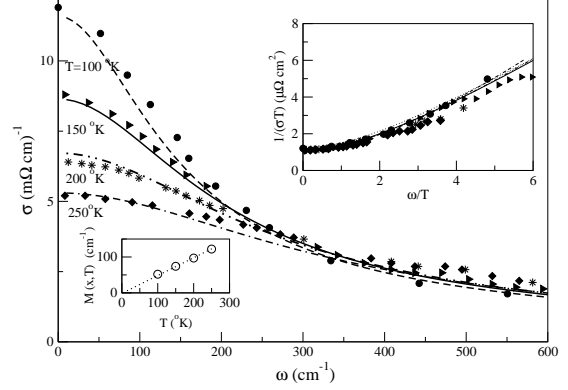


Fig. 4. Comparison between experimental optical conductivity spectra on a slightly overdoped Bi-2212 sample of Ref. [29], and theoretical spectra calculated from diagrams of Fig. 2. The intensity is chosen to fit the data with $C_\sigma = 1200(m\Omega)^{-1}\text{cm}^{-2}$, the high-frequency cutoff is $\omega_0 = 250 \text{ cm}^{-1}$, and the mass is reported in the lower inset. The upper inset reports $(T\sigma(\omega, T))^{-1}$ vs ω/T .

with the lower inset with the resulting values of $m(T)$. Again as expected on general grounds, the mass in the quantum critical region just above the QCP behaves linearly with T and in this case extrapolates to zero at $T = 0$. Furthermore, despite the many differences between LSCO and Bi2212 systems, $m(T)$ is of the same order than the one obtained for LSCO (see insets of Fig. 3). The critical nature of the excitations responsible for absorption results in a marked scaling property of $\sigma(\omega, T)$ despite the presence of ω_0 as an additional energy scale besides the mass (linearly related to T) and not only the theoretical curves display scaling, but also the experimental data show a data collapse, as shown in the upper inset.

Surprisingly, the spectra are well reproduced by the absorption from fluctuating CM only, *without* any Drude-like contribution. We find this intriguing and suggestive, although we do not have any theoretical justification for a complete suppression of the QP contribution to the conductivity in the quantum critical regime [30].

4. Conclusions

As a summary, our theory based on the occurrence of a CO-QCP around optimal doping of the cuprates accounts for a phase diagram characterized by *two* distinct crossover lines associated to the opening of pseudogaps in agreement with experiments. The theory also predicts different prop-

erties of these lines upon isotopic substitution and doping with Zn impurities. While the general features of the phase diagram are common to other theoretical proposals, experiments should eventually discriminate between different types of criticality and determine which kind of (local) order is taking place at the QCP. We provide here further support, and for the first time a unique test of our theory, through the study of the effects of the CO fluctuations on the Raman scattering. Indeed the main point of this paper is that it provides a rationale for: (a) the occurrence of anomalous temperature-dependent contributions to the Raman scattering and (b) their specific relation between the doping and the symmetry of the Raman polarizations. In this latter regard a crucial role is played by the fact that the modes excited by the Raman scattering are critical at *finite* wavevectors. Specifically the anomaly can or can not appear in the Raman spectra depending upon the direction and modulus of the critical wavevectors as deduced from independent experiments.

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References

- [1] C. M. Varma, Phys. Rev. Lett. **75**, 898 (1995); Phys. Rev. B **55**, 14554 (1997) and references therein;
- [2] C. Castellani, C. Di Castro, and M. Grilli, Phys. Rev. Lett. **75**, 4650 (1995).
- [3] For a short review see C. Castellani, *et al.*, J. of Phys. and Chem. of Sol. **59**, 1694 (1998).
- [4] J. L. Tallon, *et al.*, Phys. Stat. Sol. (B) **215**, 531 (1999); J.L. Tallon, J.W. Loram, Physica C **349**, 53 (2001).
- [5] G. S. Boebinger, *et al.*, Phys. Rev. Lett. **77**, 5417 (1996).
- [6] Y. Dagan, *et al.*, Phys. Rev. Lett. **92**, 167001 (2004).
- [7] L. Alff, *et al.*, Nature **422**, 698 (2003).
- [8] S. H. Naqib, *et al.*, cond-mat/0312443.
- [9] S. V. Borisenko, *et al.*, Phys. Rev. Lett. **92**, 207001 (2004).
- [10] A. A. Kordyuk, *et al.*, cond-mat/0405696
- [11] S. Andergassen, *et al.*, Phys. Rev. Lett. **87**, 056401 (2001).
- [12] A. Perali, *et al.*, Phys. Rev. B **54**, 16216 (1996).
- [13] C. M. Varma, Phys. Rev. Lett. **83**, 3538 (1999) and references therein.
- [14] For a review on stripes see, e.g., C. Castellani, C. Di Castro, and M. Grilli, Z. Phys. B **103**, 137 (1997) and E. Carlson *et al.*, in “The Physics of Conventional and Unconventional Superconductors”, edited by K. H. Bennemann and J. B. Ketterson (Springer, Berlin).
- [15] C. Howald, *et al.*, Phys. Rev. B **67**, 014533 (2003); M. Vershihin, *et al.*, Science **303**, 1995 (2004); McElroy, *et al.*, cond-mat/0406491.
- [16] L. G. Aslamazov and A. I. Larkin, Sov. Phys. Sol. State **10**, 875 (1968).
- [17] B. R. Patton and L. J. Sham, Phys. Rev. Lett. **31**, 631 (1973); *ibid.* **33**, 638 (1974).
- [18] D. Rubio Temprano, *et al.*, Phys. Rev. Lett. **84**, 1990 (2000).
- [19] This mechanism of “frustrated” phase separation is similar to the one independently proposed by V. J. Emery, and S. A. Kivelson, [Physica C **209**, 597 (1993)]. However, while Emery and Kivelson emphasize the one-dimensional character of the charge ordering (giving rise to “nematic” stripe phases melting upon doping into the homogeneous metallic state), our proposal specifically focuses on the second-order nature of the two-dimensional CO instability giving rise to a QCP around optimal doping.
- [20] On the contrary, CO can be strengthened by additional effects like pinning of stripes with the right periodicity by the suitable lattice structure. Such a mechanism has been proposed to be effective in $La_{1.475}Nd_{0.4}Sr_{0.125}CuO_4$, where static stripes have been observed with inelastic neutron scattering [J. Tranquada, *et al.*, Nature (1995)].
- [21] T. Honma, *et al.*, cond-mat/0309597.
- [22] M. Gutmann, *et al.*, cond-mat/0009141.
- [23] H. Ding, *et al.*, J. Phys. Chem. Solids **59**, 1888 (1998); K. Ishida, *et al.*, Phys. Rev. B **58**, R5960 (1998).
- [24] S. Takada and E. Sakai, Prog. Th. Phys. **59**, 1802 (1978); E. Sakai and S. Takada, Phys. Rev. B **20**, 2676 (1978).
- [25] See, e.g., T. P. Devereaux, *et al.* Phys. Rev. B **51**, 505 (1995).
- [26] F. Venturini, *et al.*, Phys. Rev. B **66**, 060502 (2002); L. Tassini, *et al.*, cond-mat/0406169.
- [27] See, e.g., L. Ioffe and A. J. Millis, Phys. Rev. B **58**, 11631 (1998).
- [28] S. Caprara, *et al.*, Phys. Rev. Lett. **88**, 147001 (2002).
- [29] A. F. Santander-Syro, *et al.*, Phys. Rev. Lett. **88**, 097005 (2002).
- [30] S. Caprara, *et al.*, J. of Magnetism and Mag. Mat. **272-276**, 134 (2004).